Data correlations for thermodynamic properties of HFC 134a

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ABSTRACT

Experimental thermodynamic data of the HFC134a were selected for a statistical treatment with the propose to determine an equation of state (EOS). A stable model of the EOS was found out by the many steps treaty method. The EOS had the virial row form of the compressibility factor Z. The software program based on the EOS was produced for a calculation of thermodynamic properties and tables. The calculated data are in good agreement with experimental points and the standard tables.

KEYWORDS: equation of state; method of calculatuin; thermodynamic properties; refrigerant HFC134a.

1. INTRODUCTION

The work is devoted to a complex research of the alternative substance HFC134a that corresponds to several requirements: its thermodynamic efficiency (COP) is equal to COP of CFC12 , its coefficients of ODP and GWP are low, it can substitute CFC12 in cooling equipments. Our analyses has showed that there are the experimental P-r-T- data of HFC134a in the liquid and gas phases that gives a possibility to build an united EOS for bouth phases . The virial row form inclooded coefficiens B is chosen for the EOS. The form is very convenient for programming and calculating thermodynamic functions. The coefficients B of EOS can be determined by the traditional MSQ treatment of experimental $P-\rho-T$ -data minimizing the function F - the sum of squares and solving the normal equations system . A special attention is paid to the stability of the coefficients B of the EOS to small indignations. Several stages were undertaken in the treaty to decrease the deviations E in coefficients B from the theoretical solution of the normal equations system .

2. A STABLE MODEL OF THE EQUATION OF STATE

A methodical part of the work deals with algorithm for searching of a stable model of the empirical EOS in the form of the compressibility factor :

$$Z(W, t, B) = 1 + \sum \sum b_{ij} W^{i} t^{j-1}, \quad i=1...n, \quad j=1...m,$$
 (1)

where W= Γ / $\Gamma_{\bar{n}}$, t = T_c /T, Γ_c =512 .0 kg m⁻³, T_c =374.21 K - the critical parameters.

The coefficients B in (1) can be usually calculated by a traditional MSQ treatment of experimental P-r-T-data using a minimization of the function $F = \sum \gamma_i (Z_{exp\,i} - Z(W_i))^2$. The method creates the normal equations system:

$$A \cdot B = U$$
, $A = \{a_{ij}\}, B = \{b_r\}, i = j = r = 1 \dots q, q = m \ n.$ (2)

The MSQ scheme can be considered as a single step algorithm. It gives the next solution:

$$B=A^{-1} \cdot U. \tag{3}$$

The computer result B_c , that can be produced by a standard program for solving the equation (3), deviates from the theoretical value of B and includes a vector E of deviations from B. We have investigated B_c and E in same numerical experiment. The last is based on an algorithm that includes a many steps treatment (MST). The MST method puts a set of small indignations in (2) and uses the next scheme of equations:

$$A_{i} = A + \alpha_{i} D \qquad d_{ij} = \begin{cases} 0 & i \neq j \\ a_{ii} & i = j \end{cases}$$

$$A_{l} \cdot B_{l} = U$$
, $B_{l} = A_{l}^{-1} \cdot U$, $I = 1 \dots V$, (4)

where / α_I / \leq 10 ⁻¹⁴ - a small parameter, v=39 - a number of the indignation steps.

The factor α_I D plays a role of the indignation in the equation (2). It is comparable with a mistake of a computer determination of a_{ij} . $\{B_i\}$ are determined with the help of a standard program. The computer realizations of the MST (4) deliver a rather big number ($v \approx 10^2$) of $\{B_i\}$ that can be considered as a set of chance evaluations B_c . A statistical treaty of $\{B_i\}$ are used to determine average values including \overline{B} and the dispersions $\{s_i\}$:

$$\bar{b}_r = (\sum b_r^l) / v, \quad s^2_r = (\sum (b_r^l - \bar{b}_r) / \bar{b}_r)^2) / v,$$

$$I = 1...v, \quad r = 1...q. \tag{5}$$

The start EOS model named M_0 consists of q non zero coefficients. The maximal dispersion s_{max} , r(r=z) is determined among $\{s_r\}$. The coefficient $b_r(r=z)$ is most unstable and includes the maximal deviation. It is accepted that the coefficient $b_r(r=z)$ is equal to zero. The MST gives a way for searching a stable EOS model that has \overline{B} with the small dispersions $\{s_r\}$. The next EOS model is constructed using the information about $b_r(r=z)$. Its name is M_1 . The coefficient $b_r(r=z)$ of M_1 is accepted to be equal to zero. The other q-1 non zero coefficients $\{b_r\}$ are determined using the scheme (4). The MST calculation of the next EOS models $\{M_i\}$ is continued. The numerical experiment shows that the number of zero $\{b_r\}$ increases and the dispersions $\{s_r\}$ decrease in the MST calculation. It is finished when the optimal stable EOS model is got. The optimal coefficients B give the minimization of the function F. They are stable to small computer indignations in comparison with the MSQ solution.

3. THE EQUATION OF STATE AND THE SOFTWARE PROGRAM

A practical part is connected with an adoption of the MST to an approximation of P-r-T- data of HFC 134a and continued our previous research [1]. The data base consisted of 1500 points in the liquid and gas phases and included the results of modern investigations. The EOS was built using the MST method. The coefficients B (Table 1) of the optimal model are stable to small indignations. The deviations E are considerable reduced in comparison with the model M_0 . The number of zero $\{b_i\}$ components is equal to 10. The standard deviation of P-r-T- points from EOS (1) equals to 0,11% in the density.

The expressions $P_s(T)$ and $C_{po}(T)$ were determined from the selected experimental

 $In(E_3/E_3) v = -7.6451518 f + 2.0747522 f^2 - 1.7075694 f^3 - 3.9593569 f^4$,

$$C_{p0} = -0.0513203 + 3.072249E - 02\sqrt{1}^{1/2} + 4.936996E - 03\sqrt{1}^{3/4}$$
, (6)

where $v=T/T_c$, f=1-v, $P_c=4.0515$ MPa, [T]=K, $[C_{po}]=kJ$ kg⁻¹ K⁻¹.

The equations (6) together with EOS (1) were used as a base for the software program on calculating thermodynamic properties of HFC134a. The algorithm of the determination of the function S, H, C_p , C_v and W consists of simple and clear formulas due to the virial row form of the EOS (1).

A statistical analisis and the extended scaling lows were applied to approcsimate same experimental coexisting vapor and liquid densities r' and r''. The analitical temperature dependences of the coexisting densities use the critical exponent coefficient b=0.352. The dependences are in good aggreement with the experimental points in a wide region of the critical point. The functions r'(T) and r''(T) are included in the data base for HFC 134a. together with the formulas (1,5,6).

CONCLUSION

The results of the investigation show that MSQ treaty permits to build EOS in simple form for real substances in the gaseous and liquid phases. The thermodynamic data of HFC134a determined by the elaborated program are in a good agreement with the international standard data [2] including the critical parameters. The software program can be used for determination of thermodynamic data of HFC134a with a high accuracy and in a wide region of temperatures (180-400 K) and pressures up to 40MPa.

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Table 1. Values for coefficients $\{b_{ij}\}$ of the equation of state (1)

| b11= 0.640251187E+01 | b51= 0.819369756E+01 |
|----------------------|-------------------------|
| b12=-0.258738923E+02 | b52=-0.866600563E+01 |
| b13= 0.419356975E+02 | b53 = 0.000000000E + 00 |
| b14=-0.364923177E+02 | b54= 0.279476836E+01 |
| b15= 0.153576783E+02 | b55 = 0.000000000E + 00 |
| b16=-0.271005868E+01 | b56=-0.418728556E+01 |
| b21=-0.154034363E+02 | b61 = 0.00000000E + 00 |
| b22= 0.354240716E+02 | b62=-0.679467566E+01 |
| b23= 0.00000000E+00 | b63= 0.539566613E+01 |
| b24=-0.617081568E+02 | b64= 0.240135210E+01 |
| b25= 0.605445176E+02 | b65 = 0.000000000E + 00 |
| b26=-0.179682800E+02 | b66 = 0.000000000E + 00 |
| b31= 0.329848335E+02 | b71=-0.408655677E+00 |
| b32=-0.782849759E+02 | b72= 0.364956458E+01 |
| b33= 0.442177193E+02 | b73=-0.332490887E+01 |
| b34= 0.184944282E+02 | b74=-0.690289083E+00 |
| b35=-0.182706578E+02 | b75= 0.379793926E+00 |
| b36= 0.00000000E+00 | b76= 0.138289936E+00 |
| b41=-0.260778038E+02 | b81 = 0.00000000E + 00 |
| b42= 0.536879068E+02 | b82=-0.386471079E+00 |
| b43=-0.284078904E+02 | b83= 0.482145762E+00 |
| b44= 0.00000000E+00 | b84 = 0.000000000E + 00 |
| b45=-0.982356282E+01 | b85=-0.571360510E-01 |
| b46= 0.123242990E+02 | b86=-0.126020931E-01 |
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